

EFFLUENT POLLUTION (AOX & Cr) FREE, SHRINK RESISTANCE AND DYEING PROCESSES FOR THE WOOL INDUSTRIES

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SYNOPSIS

Mechanical force is applied to wool fiber in the presence of an aqueous solution of a transition metal salt to weaken and destroy the structure of parts under the exo-cuticle (ex-CU) layer in cuticular (CU) cells so that high concentrations of transition metal can be locally introduced the under it. Then, the wool fiber is immersed in a bath containing oxidizing agents, such as hydrogen peroxide (H₂O₂) and Caroat, at an adjusted pH and temperature. The oxidizing agents are decomposed by the catalytic affect of the transition metal. The ex-CU layers in the wool fibre are peeled off by decomposition under oxygen gas pressure. Wool thus treated can be dyed even with dyes reactive for cotton, such as vinyl-sulfon types, to obtain beautiful colour 2-3 times deeper than that of dyed cotton and with excellent fastness. As a result of continued research, we have discovered that wool can be provided with various useful properties, such as antibacterial activity.

INTRODUCTION

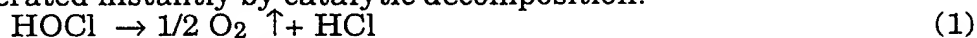
As a technology for shrinkage resistance and high-grading of wool, the authors have established a method of stripping off the ex-CU layer using the catalytic effect of transition metals and have described this process at the 7th and 8th I.W.T.R.C. (1, 2, 3).

The method consists of immersing an animal fiber in an aqueous solution of transition metal ions so that the metal ions can be absorbed by hydrophilic parts opening at the fiber surface, i.e., cell membrane complexes (CMCs) and the endo-cuticle (endo-CU) layer, and treating the fiber with an aqueous solution containing an oxidizing agent to cause catalytic decomposition by the metal ion/protein complex, thus removing the ex-CU layer and destroying the felting mechanism at the wool surface.

During the above, conventional processes are used with compounds containing chlorine (Cl) as oxidizing agents because of their strong oxidative power, which even dissolves keratin fiber.

Use of this kind of oxidizing agent inevitably results in transfer of the Cl compound into waste water. In view of the effluent limitations for AOX, it is desirable to use non-Cl based oxidizing agents, such as H₂O₂ or peroxy compounds, which are considered to be "friendly to the environment" (4).

This kind of oxidizing agent, however, has weaker oxidizing power (5). It has the strength to bleach wool, but is insufficient for removal of the ex-CU layer from it. In the case of a chlorine compound, as shown in formulae (1) and (2), gas is generated instantly by catalytic decomposition.



H₂O₂ is decomposed according to formulae (3) and (4) to generate O₂ Gas.



H₂O₂ works as a reducing agent in the presence of an oxidizing agent.
$$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 \uparrow + 2\text{H}^+ + 2\text{e}^- \quad (4)$$

Further research, however, reveals that the catalytic effect of transition metal ions is not very strong if they are absorbed by protein (6). In particular, endo-CU protein in the CU, which contains many anionic groups, tends to form chelated complexes with transition metal ions that exhibit moderated catalytic effect. Thus, it is difficult to carry out removal of the ex-CU layer using commercially available non-Cl based oxidizing agents with weaker oxidizing power.

The authors tried to apply mechanical force to the wool fibre at the time of catalyst distribution and got better results. The wool felting is a transformation of cuticular cells, which causes its bilateral structure. In the CU of wool fibre, the ex-CU layer is rigid, while the endo-CU layer is soft and weak. Thus, when strong mechanical force is applied to the fibre, considerable distortion occurs in the endo-CU parts adjacent to the ex-CU layer to the extent that the endo-CU parts are weakened and destroyed. This causes absorption of transition metal ions by these parts at concentrations higher than those in other parts.

Thus, oxidizing agents can be decomposed by the catalytic effect of transition metals. In addition, the speed of decomposition of H₂O₂ increases under the existence of (a) an alkali condition, (b) higher temperature and (c) active acid (5). Removal of the ex-CU layer is thus evolved through decomposition under oxygen gas pressure.

EXPERIMENTAL

Materials: Australian merino wool top slivers (mean fineness of 22.0 mic.) was used. This was untreated wool.

Equipment: Continuous dipping bath equipped with 8 compound rollers having an uneven surface and that can operate under water.

Treatment: A cuprous sulfate (CuSO₄) solution containing 40 ppm Cu⁺⁺ ions was prepared. (The water used throughout the experiment described below was softened water having a pH of 6.3 and was passed through an ion-exchange apparatus for industrial use.) The pH of this solution was 5.6 and it was ascertained that precipitation of Cu(OH)₂ occurs at pH 6.1. An aqueous solution of NaHCO₂ was added to the above solution to adjust the pH to 5.8.

Untreated wool (30g/m slivers) was immersed in the CuSO₄ solution at 20°C, and extension of about 20% was applied to the fiber in the above bath after 4 minutes. Then, an aqueous solution of NaHCO₃ was added to increase the final pH to 7.3 and the fibre was dehydrated in an absorbing dehydrator to adjust the water content to 60%.

NaOH solution was added to a 30% aqueous solution of commercially available H₂O₂ (H₂O₂ concentration: 35%) to adjust the pH to 9.0 with the temperature maintained at 65°C. The treated slivers were immersed in this bath for 3 minutes. Active bubbling and dissolution of copper into the bath as a brown color were observed. The wool fibre was dispersed in the solution and it was noted that the water-repellent keratin part fell away from the fibre.

These oxidation-treated wool slivers were immersed in an aqueous solution of 5g/l Na₂S₂O₅ to inhibit the effects of the oxidizing agent. After being treated by immersion in an acid bath, the pH of which was adjusted to 5.0, the wool slivers were rinsed and treated with 0.6% owf spinning oil, then dehydrated and dried.

continuous production line

semi continuous
(parts by hands)

HOCl
NI² cataizaizer
(400ppm)

H₂O₂
Cu₂ cataizaizer
(50ppm)

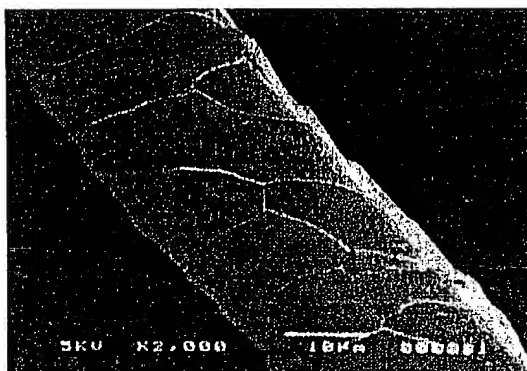


Fig I. Untreated merino wool 22M

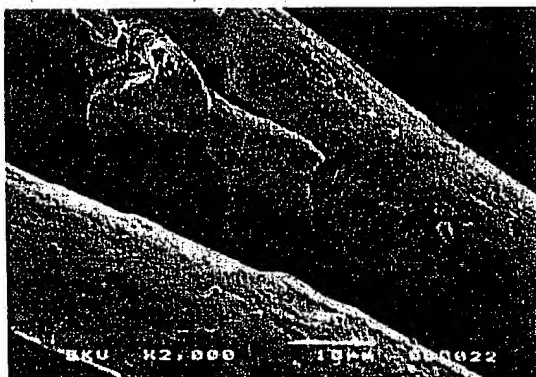


Fig II. HOCl nearly finished

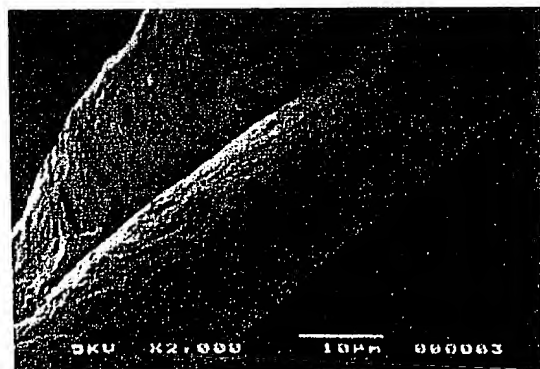
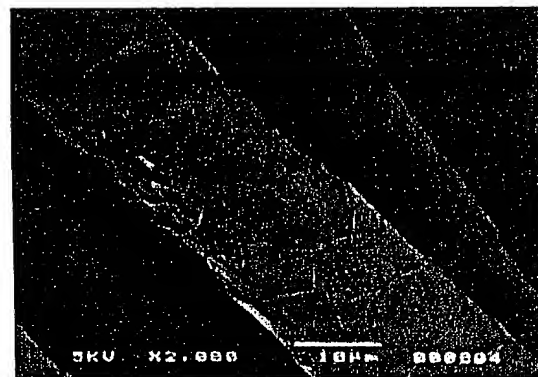
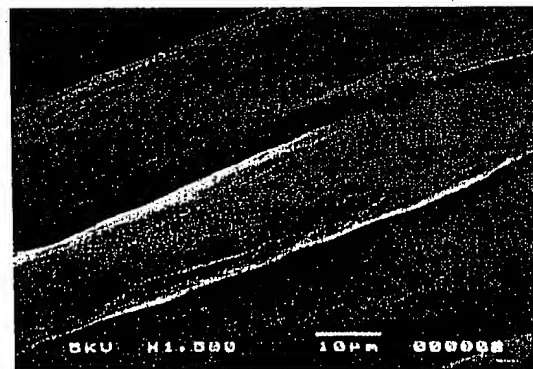


Fig III. EX - CU removed wool by Cl compound

Fig V. EX - CU removed wool by H₂O₂Fig IV. H₂O₂ nearly finished

RESULTS

- 1) The slivers thus treated were spun into 2/48N yarn using a conventional worsted spinning machine, the yarn was wound on a hank, and dyed black and navy in an injection-type hank-dyer with a Remasol-type reactive dye.
- 2) The results of fastness testing by wet rubbing was Grade 3. The fastness for acidic perspiration, alkali perspiration and washing was Grade 4.
- 3) The prepared yarn was knitted using plain stitching. The knitted product exhibited good shrinkage resistance, with an aerial shrinkage percentage of 3.2% after 5N X 5 washings as prescribed by IWS TM-31, as well as strength and dyeing fastness better than those of similar wool products.
- 4) Reference: Industrial effluence

The ex-CU process utilizing H_2O_2 is still at the stage where it is used in mini-plants, so the exact quality of industrial effluence cannot be evaluated. Thus, for reference, the effluence at factories processing wool at 150 kg/h utilizing the ex-CU removal process with a Cl-compound, which is the same as utilizing H_2O_2 , is described here. The effluence from these factories, which is mixed with the dyeing effluence generated inside the factories, is treated using the aeration method, then drained.

The results of out-flow effluence measured are (only relevant items):

1. Transition metal (Ni) (Atomic absorption spectrometry)	0.28 ppm
2. BOD (Dilution method)	1.0 mg/l
3. COD ($KMnO_4$ method)	11. mg/l
4. Total Nitrogen	18. mg/l

There is no sludge accumulation, so sludge discharge is not required.

DISCUSSION

[Machine washability, softness and comfort]

This modification removes the uncomfortable, itchy feeling peculiar to wool, the cold feeling caused by perspiration, the recurrence of felting properties, and the uncomfortably smooth feeling of shrink-resistant silicon-masked wool goods. The strength of ex-CU removed wool has been demonstrated by its use as automotive upholsteries.

This processed wool fiber has hydrophilic properties. Usually, deep-shade dyeing of wool fiber is carried out using afterchrome or Cr-complex dye. However, wool that has been treated as described above can be dyed even with reactive dyes for cotton or vinyl-sulfon group reactive dyes, to obtain a beautiful colour 2 to 3 times deeper than that of dyed cotton, and with excellent color fastness.

[Fashionable and environmentally safe]

Wool requires extensive dyeing time. However, wool that has had the ex-CU layer removed has the following advantages: easy processing; no pre-scouring; increase in types of applicable dyes; amount of dyeing assistance and dyeing time reduced by half; vivid shades; excellent color fastness; easy color discharge; manufacturing of fashionable products with minimum processing and less environmental pollution.

[Fresh feeling due to sweat absorptiveness]

Normally wool repels water. Such hydrophilic cloth as cotton, however, imparts a cool sensation due to sweat being absorbed into it after exercises, for example. Our modification covers up the shortcomings of wool by providing it with the advantages of both cloths.

Wool that has had the ex-CU layer removed more easily absorbs and vaporizes sweat than unmodified wool or cotton (8, 9).

[Antimicrobial properties]

1) The numbers of *Staphylococcus aureus* bacillus just after inoculation (A) and after culturing for 18 hours for untreated wool (B) and after culturing for 18 hours (C) for ex-CU removed wool were counted.

The following formula was derived from the results:

Difference in bacillus counts = $\log B/A - \log C/A$

The standard specified by the Textile Product Hygienic Processing Council is 1.6 or more.

Table I - Number of Initial Bacillus 1.7×10^5

Number of incubated bacillus after 18 hrs

Difference due to incubation

		/for cotton
1) Blank (cotton calico)	1.3×10^8	---
2) Untreated wool cloth	2.3×10^8	0.75
3) ex-CU removed wool cloth	8.1×10^4	4.21

The marked antimicrobial activities of wool that has had the ex-CU layer removed is proved by this comparison with the control cotton. Since *staphyrococcus aureus* causes the odor in sweat, this dedorizing property of wool that has had the ex-CU layer removed wool should be certified, if this antimicrobial activity is confirmed (10).

2) Durability of antimicrobial activity

Two types (I and II) of commercially available socks knitted from spun, dyed, woll with the ex-CU layer removed were submitted to a public organization designated by the above-mentioned council to determine the number of bacteria.

Table II - Number of Initial Bacillus 3.8×10^5

Number of Incubated Bacillus after 18 hrs

Difference by incubation

/for cotton

Socks made from wool with the ex-CU layer removed (I)

1) Blank(cotton calico)	0.4×10^5	---
2) Unwashed socks	6.3×10^{-1}	3.1
3) After 10 washings	1.6×10^0	2.7
4) After 30 washings	3.0×10^{-1}	3.4

Socks made from wool with the ex-CU layer removed

1) Blank (cotton calico)	6.3×10^2	---
2) Unwashed socks	1.0×10^{-1}	3.8<
3) After 10 washings	1.6×10^{-1}	3.6

The table shows that the antimicrobial deodorizability of wool with the ex-CU layer removed is permanent.

In addition, Cu ions were absorbed into non-processed wool and a comparison test was conducted. At just the amount of transition metals remaining in the wool with the ex-CU layer removed, there was no indication of antibacterial behavior. As a result, it was determined that antibacterial capability is not due to the catalytic transition metals utilized.

It was further determined from the obtained data that this process is effective in the formation of resistance to bacteria and fungi for gram-positive and gram-negative bacteria, which include *Pseudomonas aeruginosa*, *Escherichia coli*, *Klebsiella pneumoniae*, *Clostridium perfringens*, *Chastrominim globosum* and MRSA, as well as eumycetes cellulose-decomposing bacteria and trichophytosis bacteria, not just such standard bacteria as *Staphylococcus aureus* (11, 12, 13 14, 15).

Concerning the mechanism for expression of this natural antibacterial capability, since resistance formation efficacy is recognized for MRSA, etc., it can be considered that there is no need to worry about expression of new bacteria resistant to such medicines as antibiotics, but efforts are now being made to confirm this.

[Additional chemical properties]

1) It has already been proved that wool with the ex-CU layer removed rapidly absorbs considerable quantities of sulfur dioxide (SO₂) in the same manner as untreated wool (16).

2) A test for desorption of caproic acid, an odoriferous compound, was performed on wool with the ex-CU layer removed, polyester and polyacrylic fibers. The test results indicate that deodorizing activity in wool with the ex-CU layer removed is extremely high (17).

[Wound dressing material]

[Evaluation as wound dressing material]

Cloth from wool with the ex-CU layer removed has superior effect on early healing of wounds to hog skin, which is widely used by clinicians in hospitals, and has stimulating effects on skin regeneration. A stretchable wound-coating material that can be manufactured using wool industry technologies can be supplied for a wide field of applications (18, 19).

[Special features as clothing]

Sheep wool has a "pertinency to nature" for maintaining the homeostasis of the body by neutralizing external harmful matter.

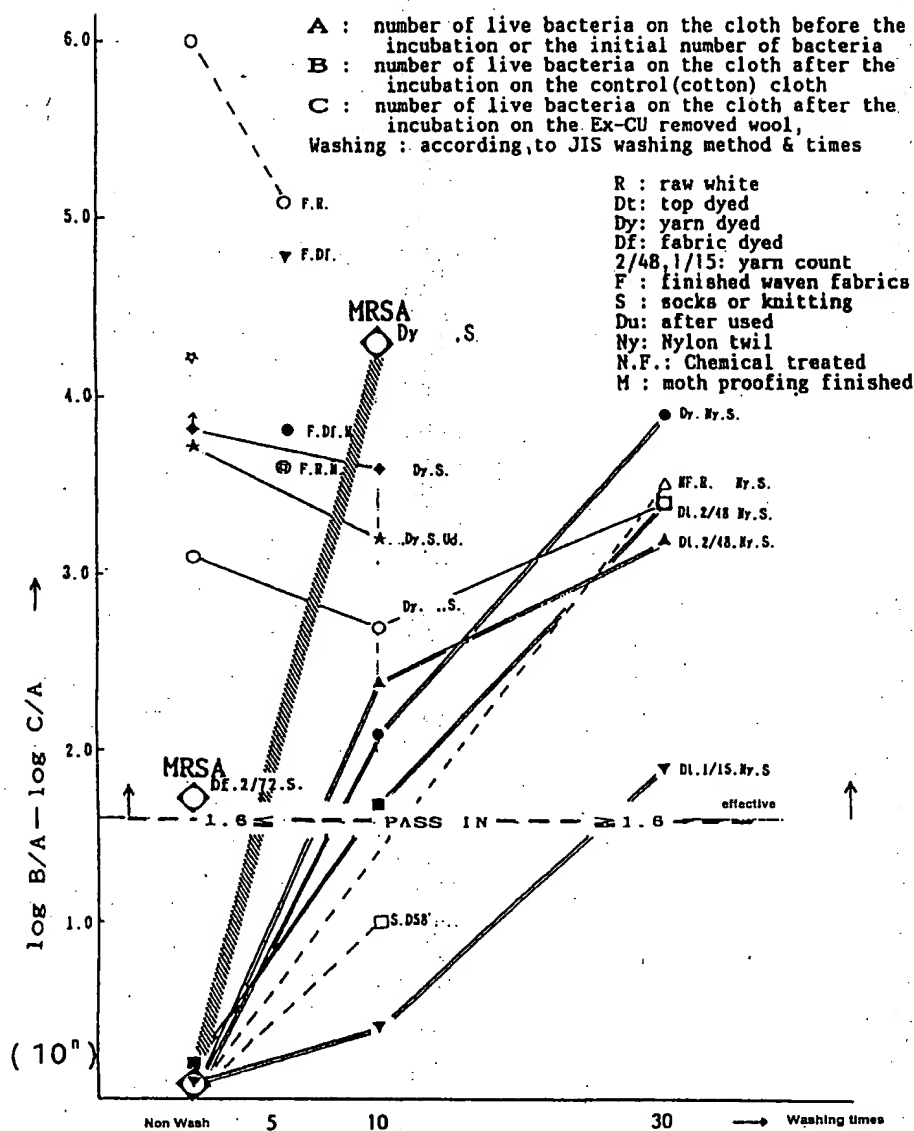
Bacterio-Static Ability of Exo-cuticle Removed Wool

Bacteria: *Staphyrococcus aureus* ATCC 6538P 37° X 18h incubation

MRSA: methicillin resistant *Staphyrococcus aureus*

Testing method: Bcillus counting method (SENI SEIHIN EISEIKAKO Association)

Difference by Exo-cuticle removed wool(Ex-CU removed wool) cloth(D-Imp) was caluculated as follows: $(D-Imp) = \log B/A - \log C/A$
(previously Standard of bacterio-static effect is more than 1.6 or D-Imp)



CONCLUSIONS

Nature is sometimes immensely complex. If only valuable matter is picked out from these materials and the apparently irrelevant disregarded, we will eventually be inundated by heaps of refuse. Most of the current social problems are the consequences of this simplistic approach.

In the future, industry has to aim at manufacturing products that enhance living standards by maximizing natural functions. Functions desirable for human beings can be found even in fibre made from the wool of sheep living in the natural world.

Body hair, such as wool, is what the animal itself produces as a barrier over the skin to maintain its individuality. When conventional dyeing methods are applied to wool, the finished color at the tip of the strands appears to be different from that of other parts because the ex-CU layer came off. Noting this, we performed an experiment to remove the ex-CU layer from the entire textile. Then an unexpected natural function, which can be called the barrier function, as mentioned above, appeared.

(Note): As described previously, trial production at a series of mini-plants to improve utilization of H_2O_2 has started. It has already been confirmed through partial performance that this improved product can obtain almost the same or better level of performance that Cl-compound improved wool has.

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REFERENCES

1. H. Hojo: Proc. 7th Inter. Wool Res. Con. Tokyo. IV, P322 (1985)
2. H. Hojo et al.: Proc. 8th Inter. Wool Res. Con. Christchurch. IV, P390 (1990)
3. H. Hojo et al.: JP No. 1164876, & JP No. 1454499, priority Sep. 22, 1980
4. T. Shaw: Proc. 8th Inter. Wool Res. Con. Christchurch, IV, P533-547 (1990)
5. J. Cegarra & J. Gacen: Wool Science Review 59. Sep, 1983
6. Kazuhiko FUKATA: Tex. Res. J., July, 1989, p405-410
7. H. Hojo: J.P.A. No. H7-78633, J.P.A.No. H6-125092, J.P.A. No.H-6-293502
8. N. Mitui et al.: Jpn. J. Biometeor, 23, p35-42 (1986)
9. H. Gocho & T. Nakajima: SEN-I GAKKAISHI 50 1994, P-321-324
10. H. Hojo et al.: SEI-I GAKKAI PREPRINTS p S-136 (1992)
11. M. Suzuki et al.: 40th Japanese Association of School Health, Nov. 25-26, 1993
12. M. Suzuki et al.: Preprints, 13th Allied Fiber Sie.Jpn (1993)
13. M. Suzuki et al.: SEN-I GAKKAI PREPRINTS (1994) p S-2
14. M. Suzuki et al.: 41th Japanese Association of School Health (1994)
15. N. Minagawa et al.: 35th Annual Meeting of the Japan Society of Air Pollution, MORIOKA-CITY (1994)
16. I.W.S., I.T.C. Report (1987)
17. I.W.S., I.T.C. Report (1990)
18. J. Koga et al.: SEN-I GAKKAI PREPRINTS 1991 p C-183
19. H. Hojo: USP No. 5304378 Apr. 19 1994, Priority Data July 26, 1990, Japan